

{NASA-TM-100301} AN EVALUATION OF RAIN
CHEMISTRY DATA FOR THE JOHN F. KENNEDY SPACE
CENTER, FLORIDA AND THE UNIVERSITY OF
CENTRAL FLORIDA, ORLANDO (NASA) 26 p
Avail: NTIS HC A03/MF A01

N87-25635

Unclas
0083876

CSCL 13B G3/45

An Evaluation of Rain Chemistry Data for the John F. Kennedy Space Center, Florida and the University of Central Florida, Orlando, Florida

October 1986



National Aeronautics and
Space Administration

An Evaluation of Rain Chemistry Data for the John F. Kennedy Space Center, Florida and the University of Central Florida, Orlando, Florida

Brooks C. Madsen, Ph.D.
Department of Chemistry, University of Central Florida
Orlando, Florida

Thomas W. Dreschel
C. Ross Hinkle, Ph.D.
The Bionetics Corporation, Kennedy Space Center, Florida

October 1986

This work was performed for the NASA Biomedical Operations and
Research Office, John F. Kennedy Space Center, Florida, under
Contract NAS10-10285

TABLE OF CONTENTS

SECTION	PAGE
Table of Contents.....	1
Abstract.....	11
List of Figures.....	111
List of Tables.....	1v
Acknowledgements.....	v
Product Disclaimer.....	v
I. INTRODUCTION.....	1
II. METHODS AND MATERIALS.....	1
A. UCF/KSC Monitoring.....	1
B. Contractor Monitoring.....	4
C. Data Quality and Comparability.....	4
III. RESULTS AND DISCUSSION.....	4
IV. CONCLUSIONS/RECOMMENDATIONS.....	13
V. LITERATURE CITED.....	17

ABSTRACT

Concern over the effects of Space Shuttle launches prompted the initiation of a rather intense environmental monitoring program in July 1977. The program included a precipitation monitoring network with 13 precipitation collection sites which were operated for various time periods to baseline precipitation chemistry at the John F. Kennedy Space Center (KSC). One additional site was also established as a remote background site on the University of Central Florida (UCF) campus near Orlando, 30 miles west of KSC. One of the 13 sites was converted to a National Atmospheric Deposition Program (NADP) station in August of 1983. Collections and analyses of samples were performed using a number of methodologies during the monitoring period. An evaluation of the data for comparability and utility for acid rain research was performed using the anion/cation, measured conductivity/calculated conductivity, Cl/Na, and Mg/Na ratios. Data collected at all KSC sites between 1977 and 1981, from 1983 to 1985 at the NADP site and at UCF to 1985 are comparable and appropriate for determining acid rain trends. Examination of those comparable data showed a fairly stable pH between 1977 and 1982 and an increase of 0.2 pH units which was observed as an incremental increase between 1982 and 1983 at KSC and UCF. The pH has remained again stable for 1984 and 1985. There is no indication of any adverse impacts from Shuttle launches to rain chemistry.

LIST OF FIGURES

	PAGE
Figure 1. Locations of University of Central Florida and Kennedy Space Center rainwater sampling sites indicating length of time operated.....	2
Figure 2. Annual weighted average concentrations of major ions in rain at three sites.....	5
Figure 3. Temporal trends in monthly weighted average hydrogen ion concentrations in rain at the University of Central Florida.....	12

LIST OF TABLES

	PAGE
Table 1. Typical parameters used to evaluate data quality.....	3
Table 2. Rainfall chemistry summaries for Kennedy Space Center during recent years.....	8
Table 3. Annual and cumulative rainfall chemistry summaries for the University of Central Florida...	9
Table 4. Comparison of monthly volume weighted average pH based on event field, event laboratory, weekly field, and weekly laboratory records for samples collected at the KSC CIF site during 1984 and 1985.....	10
Table 5. Ionic predictors of acidity in rain based on a stepwise regression model.....	14
Table 6. Linear regression model of the relationship between various monthly weighted average concentrations in rain at UCF and KSC site 13/ NADP.....	15

ACKNOWLEDGEMENTS

This project was conducted under the direction of Dr. William M. Knott, III, Biological Sciences Officer and Dr. Albert M. Koller, Jr., Chief, Programs and Planning Office, Biomedical Operations and Research Office, John F. Kennedy Space Center (KSC) under NASA contract no. NAS10-10285.

We thank Robin Cone, University of Central Florida (UCF), and Tami Skidmore of The Bionetics Corporation for typing assistance, numerous UCF students for chemical analyses support, employees of The Bionetics Corporation Long-term Environmental Monitoring and Research Program for field assistance and Terry Layer of EG&G Florida, Inc. for graphics assistance.

PRODUCT DISCLAIMER

This report, in whole or in part, may not be used to state or imply the endorsement by NASA or by NASA employees of a commercial product, process or service, or used in any other manner that might mislead.

I. INTRODUCTION

Interest in the problem of acid precipitation has increased over the last several decades. Typically, sulfuric and nitric acids have been of primary concern, arising from sulfur and nitrogen oxide precursors which are products of combustion processes. Nation-wide efforts such as the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) (Robertson and Wilson 1985) and state-wide efforts within Florida such as the Florida Coordination Group Acid Rain Study (ESE 1982) have provided much information on the extent and severity of this problem.

Concern over hydrochloric acid (HCl) produced by the Solid Rocket Boosters (SRB's) of the Space Transportation System (STS) prompted a rather intense precipitation monitoring program (Madsen 1981) and a local network of 13 sites (Figure 1) to monitor the presence of acid rain was established by B.C. Madsen of the University of Central Florida (UCF) at the John F. Kennedy Space Center (KSC) in 1977 as part of an environmental monitoring and research program. Research involving the comparison of sampling interval lengths (Madsen 1982) and of coastal versus inland sites (Madsen 1984) were included as part of this monitoring program. Involvement of UCF in the KSC monitoring program ended in late 1981. One site was continued at KSC within 1 km of the original sites (13) under NASA contracts to independent contractors through 1985. A NADP station was established at KSC at the same site in August of 1983. Two other research sites were operated for one year each starting in early 1984 (Figure 1).

A monitoring site was established at the UCF campus in 1977 as part of the UCF/KSC program and that site has been operated continuously since that time. The purpose of this report is to summarize data gathered at KSC and UCF through 1985 with emphasis on synthesis of the eight year data set. Data quality has been evaluated for individual samples. The utility of this monitoring effort will be evaluated with respect to the following: 1) input for management and operational decision making, 2) acid deposition data base for research efforts, 3) preliminary assessment of data as a long-term environmental data base for KSC and east-central Florida, and 4) recommendation for future program focus with respect to continued monitoring.

II. METHODS AND MATERIALS:

A. UCF/KSC Monitoring

Rain samples were collected at all sites (Figure 1) as wet-only samples utilizing Aerochem-Metrics precipitation collectors. Typically, samples were collected as daily samples on Tuesday through Friday and as three-day samples on Monday. Samples were analyzed and archived under refrigeration until the data could be evaluated and verified. Data quality was evaluated by examining

Figure 1. Locations of University of Central Florida and Kennedy Space Center rainwater sampling sites indicating length of time operated.

MONITORING SITES

1977—1986

18

1977—1981

01, 13, 14, 16, 19

1978—1979

02, 03, 05, 06, 08, 10, 11, 12

CIF

1981—1985

PAD 39A, UF MARSH

1984—1985

NADP

1983—1986

SLF (VOLUME ONLY)

1981—1986

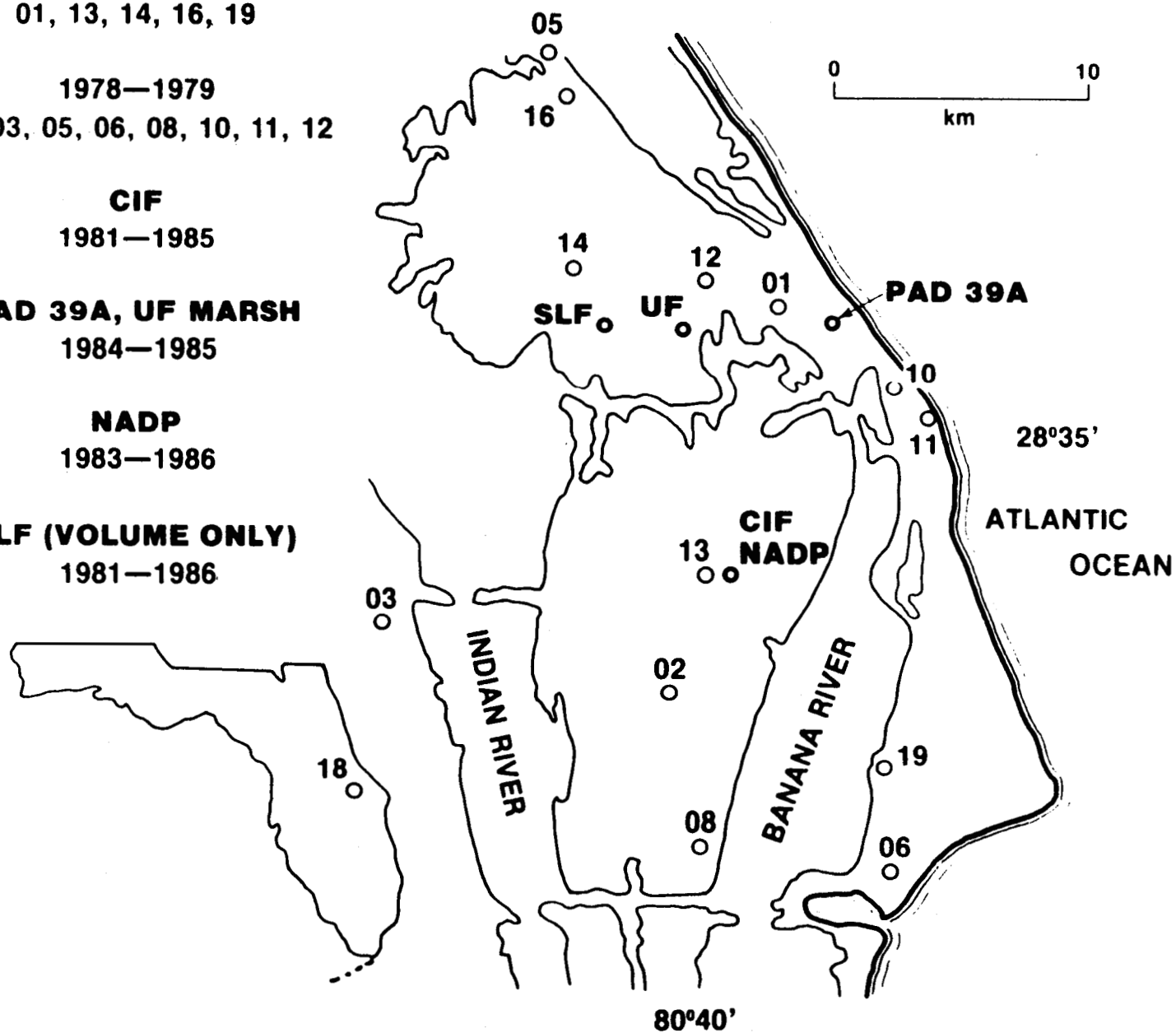


Table 1. Typical parameters used to evaluate data quality.

Parameter	Expected Value
Anion/cation (eq./eq.)	1.0 ± 0.2
Measured/calculated conductivity	1.0 ± 0.2
Cl/Na (eq./eq.)	$1.16 \pm 0.2^*$
Na/Mg (eq./eq.)	$0.2 \pm 0.2^*$

*Expected value in marine environment. Considerable latitude must be given to these values when concentrations are low (e.g., below 0.3 ppm Na^+).

a number of diagnostic ratios (Table 1): anion/cation, measured/calculated conductivity, Cl/Na, and Na/Mg, on an individual sample basis (Galloway and Likens 1978). A more detailed description of the program was given elsewhere by Madsen (1981, 1981a).

B. Contractor Monitoring

Little information is available on the procedures used during 1982 through 1984 but it is assumed that those of the UCF/KSC monitoring program were continued. One site was operated in this fashion through 1984 with few procedural changes that relate to sample collection. During 1984 and 1985, polyethylene bucket liners were used in the wet-only collection bucket to avoid the need for bucket washing and to minimize contamination through handling. In early 1984, two stations were established at research project sites to provide background deposition measurements based on collection of weekly samples. Chemical analysis was performed by various groups from November 1981 until December 1985. After collection, sample conductivity and pH were determined on a small portion of sample and the remaining sample was transferred to a clean sample bottle and submitted to the laboratory for chemical analysis. The NADP site was selected and was operated according to NADP protocol (Bigelow 1984 and Bigelow 1982) and sample handling and analysis quality were carefully monitored using round-robin and check samples and data evaluation (NADP 1984). Site operators were trained by the NADP/NTN central analytical laboratory personnel and periodic site visits were made. A more detailed description of sites and procedures used during 1983-1984 are discussed in a report by Dreschel (1984). Rainfall amounts were taken from Belfort rain gages at three sites. Rainfall amount data was also obtained from the Shuttle Landing Facility (SLF) weather station (Figure 1).

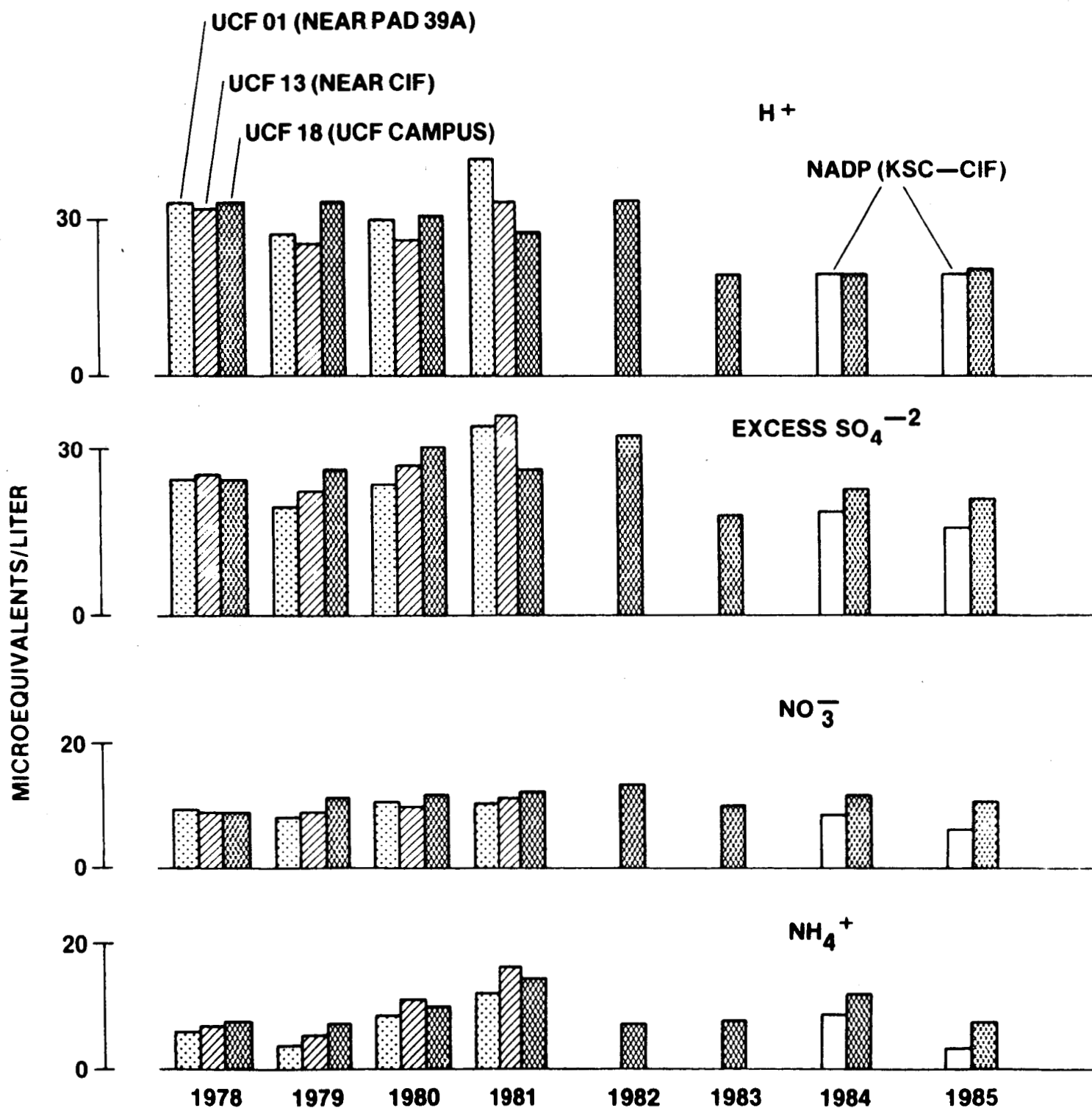
C. Data Quality and Comparability of the 1977 through 1985 Data Set

The calculation of the conductivity/calculated conductivity, anion/cation, Cl/Na and Na/Mg ratios were performed on data for individual samples and were used to evaluate data quality and comparability (Galloway and Likens 1978). Highly contaminated samples were not included in data evaluations.

III. RESULTS AND DISCUSSION

Annual volume-weighted mean concentrations of selected major ionic species present in rain for 1977 through 1985 from two sites which were part of the original UCF/KSC network, the UCF site and the current KSC NADP site, are presented in Figure 2. The complete acid deposition data base which covers the period

Figure 2. Annual weighted average concentrations of major ions in rain at three sites.



from 1977 through 1985 has been archived at KSC using the NASA Biomedical Operations and Research Office computer system.

Although sample collection methodology has remained essentially constant from 1977 to 1985, an important difference exists in the archived data base for the corresponding time period. All data obtained as part of the UCF/KSC monitoring program during 1977 through 1981 and data collected at UCF during 1981 to 1985 were subjected to rigorous quality assurance which includes quality control and data evaluation prior to archiving. These efforts were used to ensure the overall high quality of data regardless of intended end use. No attempt was made to incorporate quality assurance into data collection for any other acid deposition samples collected at KSC except those which are part of the NADP program. Recent attempts described later in this report have been made to evaluate the reliability of the data collected without necessary quality assurance.

In general these more recent data sets (1981-1985) are characterized by incomplete data, e.g., concentrations for all anions and cations in individual samples are not available, either because of omission in the chemical analysis scheme or because detection limits for the methods of analysis were too high. It has been shown that the composition of rainfall at UCF is similar to that for samples collected at KSC (Madsen 1984). This conclusion, based on data collected during 1977 through 1981, has been projected in qualitative fashion to assist in the diagnosis of data errors in the KSC data collected since 1981. Data evaluation has resulted in the following observations:

- 1) Chemical analysis data obtained from November 1981 through December 1982 are generally of acceptable quality, however, the rainfall amounts are missing which prohibits utilization of data in applications where environmental loading is of importance and precludes calculation of weighted mean concentrations.
- 2) Data from January 1983 through June 1983 show consistently and unreasonably high values for sample pH and chemical procedures have apparently introduced errors into a majority of the samples which negate data validation efforts.
- 3) Methods of analysis used during the period June 1983 through 1985 for CIF event samples and project related samples (Pad 39A, UF marsh) yield data characterized by large random errors because many measurements were performed at or near unacceptably high detection limits (Galloway and Likens 1978, NADP 1984). Chloride and sulfate determinations were prime examples. It also appears that many pH determinations were in error which leads to gross over estimation of acidity.

- 4) Data generated as part of the NADP and UCF programs are of high quality. In addition "field" pH measurements made at KSC from mid-1983 through 1985 were generally consistent with NADP and UCF data and therefore form the basis for a valid but limited data set.

Table 2 presents a comparison of historic data from three sites (Madsen 1981), with data obtained during 1984 at sites near three original sites. In general pH levels measured in 1984 were approximately 0.2 units higher than the annual 1977-1981 mean pH value. The higher pH values account for much of the deposition decrease of approximately 50 percent. The pH and acid deposition data which were available for the period 1978-1985 at UCF showed these same differences and reflected a "real" change in pH and deposition. These data are presented in Table 3 along with individual ion concentration and selected deposition data.

The data presented in Table 4 summarize pH values obtained from samples collected at the KSC CIF site during 1984 and 1985. Annual mean field pH determined from CIF event samples and weekly NADP samples were in excellent agreement with the 1984 and 1985 annual mean pH determined from samples collected at UCF. It has previously been shown that no statistically significant difference in pH existed between samples collected at UCF and at KSC during 1977-1981 (Madsen 1984). A paired sample t-test applied to recent (1984-1985) UCF and NADP field monthly weighted average pH suggests that no statistically significant difference exists. The NADP laboratory pH values were greater during nine months out of the two year period than the NADP field pH values and resulted in a field determined acidity which is 23 percent greater than laboratory acidity. Verry (1983) has reported differences in NADP field acidities which are up to 10 times greater than laboratory acidities for rainfall and snow samples collected in Minnesota. These differences have been attributed to sample decomposition and/or transit contamination problems. Samples collected at UCF during 1985 and stored at room temperature or at 4°C for extended periods have shown no appreciable changes in pH. This observation is consistent with previous data from 1980. The very low CIF event laboratory pH data obtained during 1984 and 1985 are contrary to all documented changes which have been reported for precipitation samples caused by contamination during transit or decomposition during extended storage. The annual mean acidity which is 140 percent and 99 percent greater for 1984 and 1985, respectively, than a conservative estimate based on NADP laboratory pH values for the corresponding periods appears to be an unacceptably high estimate which in all probability has resulted from the general lack of an acceptable quality assurance program.

Dramatic changes in rainwater pH have been described for samples collected as part of the NADP and MAP3S monitoring programs where pH is first measured in a field laboratory shortly after the end of a specified sampling period and later in a central analytical

Table 2. Rainfall chemistry summaries for Kennedy Space Center during recent years.

Site Time Period	UCF01 1978-81	PAD39A 1984*	UCF12 1978-79	UF MARSH 1984*	UCF13 1978-81	CIF EVENT 1984*	NADP 1984	NADP 1985
cm/yr	110.9	111.2**	138.6	99.0***	114.2	122.1	122.1	116.2
pH	4.45	4.74	4.55	4.83	4.52	4.71	4.71	4.83
Deposition H (meq/m ² -yr)	39.3	17.8	39.1	13.8	34.4	23.8	20.8	16.8
Deposition NH ₄ (meq/m ² -yr)	10.7	5.8	7.2	2.4	13.8	4.0	5.4	2.1
Deposition NO ₃ (meq/m ² -yr)	13.9	10.1	15.6	9.0	14.2	10.1	10.6	8.8
Deposition SO ₄ (meq/m ² -yr)	39.4	54.8	41.8	45.5	40.2	51.8	30.4	22.7
H (ueq/L)	35.4	18.1	28.2	14.7	30.2	19.3	19.3	14.8
Na (ueq/L)	52.8	242	60.7	100	40.9	59.2	71.7	34.6
K (ueq/L)	1.8	7.7	1.9	4.4	1.9	2.1	2.3	1.1
Ca (ueq/L)	8.3	21.1	6.9	10.5	9.8	7.0	8.7	7.4
Mg (ueq/L)	12.0	58.7	14.2	20.0	10.0	14.2	17.2	8.9
NH ₄ (ueq/L)	9.6	11.2	5.2	4.1	12.1	4.5	5.0	3.0
Cl (ueq/L)	57.8	314	64.5	91.3	43.7	85.7	75.4	41.8
NO ₃ (ueq/L)	12.6	10.3	11.3	8.7	12.4	8.2	9.8	7.8
SO ₄ (ueq/L)	35.5	56.2	30.2	44.0	35.2	42.0	28.2	20.0
excess SO ₄ (ueq/L)	29.6	33.4	23.6	36.1	30.8	36.3	19.6	16.0

*Values are based on all samples analyzed, however, less than 50% of the samples meet all data validation criteria. The reported pH values are from KSC field measurements.

**Time period January 19, 1984 - December 31, 1984.

***Time period March 1, 1984 - December 31, 1984.

Table 3. Annual and cumulative rainfall chemistry summaries for the University of Central Florida.

Time Period	1978	1979	1980	1981	1982	1983	1984	1985	7/77-12/85
cm rain/12 months	135.2	157.8	99.6	93.8	152.8	152.4	128.2	178.5	140.9
pH	4.47	4.49	4.54	4.54	4.47	4.72	4.71	4.66	4.55
Deposition H (meq/m ² -yr)	45.4	50.6	29.0	27.2	51.8	29.0	24.7	39.2	38.5
Deposition NH ₄ (meq/m ² -yr)	11.7	13.8	12.0	15.3	15.2	11.1	11.1	15.8	13.0
Deposition NO ₃ (meq/m ² -yr)	14.6	21.3	13.6	13.9	24.7	18.6	17.7	23.8	18.3
Deposition SO ₄ (meq/m ² -yr)	38.9	45.2	31.8	30.4	55.8	32.9	35.8	45.6	39.0
H (ueq/L)	33.6	32.1	29.1	29.0	33.9	19.1	19.3	22.0	27.6
Na (ueq/L)	14.8	21.0	12.8	25.4	14.0	20.9	28.2	23.0	20.0
K (ueq/L)	1.5	1.2	0.8	1.0	0.4	1.3	0.7	1.0	1.0
Ca (ueq/L)	6.9	8.4	11.2	11.4	12.1	9.2	11.1	9.4	9.8
Mg (ueq/L)	4.0	5.6	3.2	7.0	3.9	5.6	7.5	5.9	5.3
NH ₄ (ueq/L)	8.6	8.7	12.1	16.3	10.0	7.3	8.6	8.8	9.6
Cl (ueq/L)	15.9	24.6	13.9	29.8	18.0	25.4	33.8	29.0	23.9
NO ₃ (ueq/L)	10.8	13.5	13.6	14.8	16.1	12.2	13.8	13.3	13.4
SO ₄ (ueq/L)	28.8	28.6	32.0	32.4	36.3	21.6	27.9	25.5	28.6
excess SO ₄ (ueq/L)	27.2	26.2	30.6	29.5	34.9	19.2	24.6	22.8	25.3

Table 4. Comparison of monthly volume weighted average pH based on event field, event laboratory, weekly field, and weekly laboratory records for samples collected at the KSC CIF site during 1984 and 1985. Values in parenthesis represent difference in acidity compared to NADP determined acidity.

	CIF EVENT				WEEKLY NADP STATION			
	Field 1984	pH* 1985	Lab 1984	pH** 1985	Field 1984	pH* 1985	Lab 1984	pH*** 1985
January	4.25	4.74	4.37	4.74	4.49	5.13	4.48	5.72
February	4.83	4.64	4.79	4.35	5.04	5.04	4.96	5.34
March	5.20	5.18	4.87	5.45	4.94	5.09	5.04	5.42
April	5.78	4.98	5.31	4.51	4.94	4.85	4.82	5.15
May	5.00	4.27	5.08	4.32	5.00	4.54	5.31	4.58
June	4.28	4.46	4.05	4.26	4.17	4.62	4.36	4.77
July	4.90	4.59	4.12	4.64	4.79	4.42	4.90	4.50
August	4.23	4.54	3.84	4.65	4.28	4.48	4.42	4.60
September	4.97	5.10	4.84	5.05	4.70	4.85	4.73	5.23
October	4.64	4.91	4.58	4.62	5.04	4.80	5.11	4.90
November	4.96	4.82	4.98	4.57	5.15	4.75	5.16	4.72
December	4.33	5.01	4.62	4.28	4.44	4.77	5.05	5.15
Annual	4.71	4.67	4.42	4.53	4.71	4.68	4.80	4.83
Mean	(+23%)	(+45%)	(+140%)	(+99%)	(+23%)	(+41%)		

*Performed at KSC.

**Performed at contractor laboratory.

***Performed by NADP central analytical laboratory.

laboratory (Keene and Galloway 1984). The presence of weak acids which are slowly decomposed is currently proposed to account for the pH changes which have been observed.

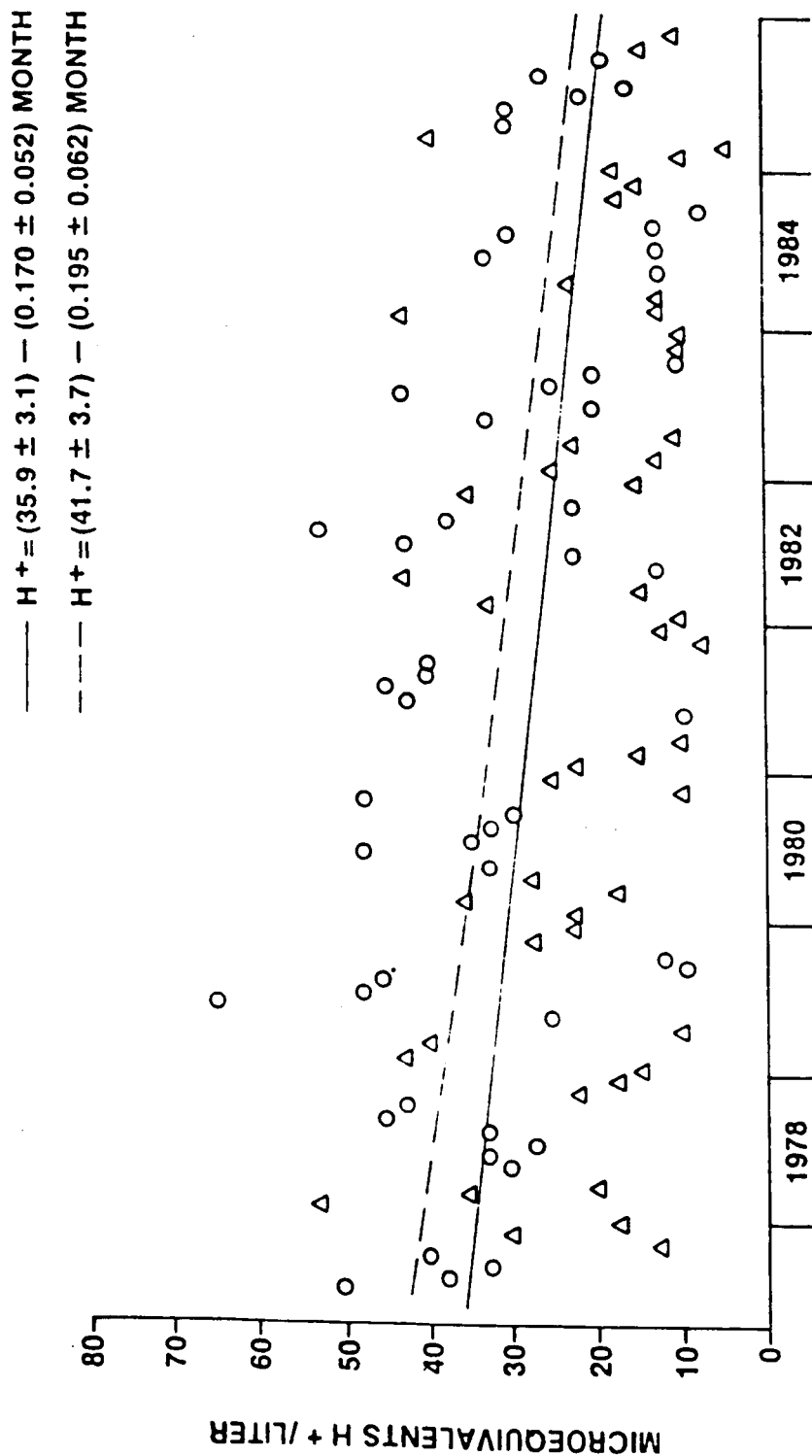
The evaluation of trends with time associated with acid precipitation in the U.S. has been limited because of a general lack of data covering periods prior to the 1980's. Several investigators have used the linear regression slope and its standard deviation or the linear regression correlation coefficient to evaluate trends. Because precipitation data are quite variable and dramatic changes with time are seldom observed over the few years where data are available, documentation of trends is generally not forthcoming. Pratt, et al. (1983) evaluated Minnesota rain over a four year period. Galloway and Likens (1981) have subjected the 15 year records from Hubbard Brook, New Hampshire to the same treatment and observed trends when seasonal treatment of monthly sulfate and nitrate concentrations are considered. Likens, et al. (1984) have considered the 1964-1982 annual weighted average concentrations from Hubbard Brook in similar fashion and found evidence to suggest that trends for H^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} , and Cl^- may exist.

The MAP3S/RAINE Research Community (1982) presented a comprehensive statistical overview intended as a starting point for various interpretive studies of a four year precipitation chemistry data base. Delineation of temporal features included linear regression analysis of event data with correlation coefficients and probabilities reported to assess the strengths and confidence levels of possible trends.

Hidy, et al. (1984) have proposed a qualitative "boxplot" approach to trend evaluation for ill-defined data and conclude that evidence for downward trends in sulfate and pH and upward trends in nitrate and ammonium ion concentrations for Hubbard Brook and U.S. Geological Survey (USGS) data for the period 1965-1980 do exist. The approach taken by Bilonick and Nichols (1983) utilizes autoregressive integrated moving average processes to evaluate temporal changes in acidity based on the same USGS data set and concluded that no evidence exists to support a conclusion of long-term change in the mean acidity level.

Evaluation of the UCF precipitation chemistry data base summarized as monthly weighted averages for the period July 1977 to December 1985 using a linear regression model reveals the indication of a downward trend in acidity. The data and resulting linear regression equation are presented in Figure 3. Evaluation of data for the other major cations (Na^+ , K^+ , Mg^{2+} , NH_4^+) and major anions (Cl^- , NO_3^- , SO_4^{2-}) do not reveal trends ($P < 0.05$). When monthly deposition of acidity, etc. (cm x concentration) were treated in similar fashion no indication of trends ($P < 0.05$) was apparent. No indication of trends was

Figure 3. Temporal trends in monthly weighted average hydrogen ion concentrations in rain at the University of Central Florida.



- Δ INDICATE WINTER (NOVEMBER—APRIL) VALUES
- INDICATE SUMMER (MAY—OCTOBER) VALUES
- IS THE REGRESSION LINE USING ALL MONTHLY VALUES, $n=102$, $p=0.013$
- IS THE REGRESSION LINE FOR SUMMER ONLY VALUES, $n=52$, $p=0.011$

apparent when site 13/NADP data were considered as a collective set then subjected to the same evaluation as the UCF data set.

Precipitation acidity is the cumulative result of contributions of many acidic and basic compounds which are present in the atmosphere. Acidity of rain at KSC and UCF was highly correlated with nitrate concentration and with sulfate concentration (Madsen 1981, 1984). Stepwise regression analysis of the UCF data (Madsen 1984, 1985) revealed a model which showed the contributions of nitrate and sulfate concentrations as measures of neutralizing or basic cations. Summaries of the stepwise regression analysis and individual ion correlations are presented in Tables 5 and 6. The trend in acidity over time had been observed in the presence of moderate monthly fluctuations while no other individual ion concentrations exhibited or suggested a similar trend. In fact, the decrease in acidity was readily observed to be an incremental drop during 1983, 1984, and 1985 compared to 1978-1982 as summarized in Table 3. This type of change was also observed to a lesser extent for sulfate but not for nitrate. These results should therefore be cited with appropriate qualification and reservation due to the relatively short record duration.

IV. CONCLUSIONS/RECOMMENDATIONS

Careful evaluation of the existing acid precipitation data base for KSC and UCF has revealed that portions are unsuitable for use independently and should not be included for use in other studies. In general, those data obtained through involvement of UCF, NADP, and KSC field measurements made since August 1983 are of suitable quality. It is recommended that activities at KSC be streamlined to include only the NADP site for routine chemistry monitoring purposes. If special study sites are to be activated then external service laboratories should not be used to analyze samples unless rigorous quality assurance/quality control programs such as those used by NADP can be implemented and enforced. The NADP protocol stipulates weekly sampling intervals and it is recommended that daily sampling be continued at the UCF site. This will ensure that data from a single site which has been a part of the monitoring program since its inception will be available to better assess trends in composition. The temporal resolution obtained with daily sampling can form the basis for future incorporation of meteorological interpretations and will result in a smaller fraction of samples "lost" through severe contamination.

Management and operational justification for the atmospheric deposition monitoring program comes from a number of areas. Studies have been conducted to investigate the possibility of recovering storm water for recycling purposes (Heaney, et al. 1984, Jones 1986). Knowledge of the quality and quantity of rainfall available for use will be of great value in evaluating the potentials of the project. Effects of acid rain on materials

Table 5. Ionic predictors of acidity in rain based on a stepwise regression model.

	1978	1979	1980	1981	1982	1983	1984	1985
UCF	xsSO ₄ -NH ₄ NO ₃ -Ca	xsSO ₄ -Ca -Mg NO ₃	xsSO ₄ -NH ₄ -Ca NO ₃	xsSO ₄ -NH ₄ -Ca NO ₃	xsSO ₄ -NH ₄ NO ₃ -Ca	xsSO ₄ -NH ₄ NO ₃ -Ca	NO ₃ -Ca xsSO ₄ -NH ₄	xsSO ₄ -Ca NO ₃ -NH ₄
number of samples	67	81	77	67	95	74	68	90
r ²	0.89	0.99	0.94	0.91	0.94	0.88	0.96	0.80
KSC13/NADP*	xsSO ₄ -Ca NO ₃ -NH ₄ -K	xsSO ₄ -Ca NO ₃ -NH ₄ -K	xsSO ₄ Na -Mg -Ca NO ₃ -NH ₄	NO ₃ -Ca xsSO ₄ -NH ₄			NO ₃ -Ca -NH ₄ xsSO ₄	xsSO ₄ -Ca NO ₃ -NH ₄ Na -Mg -Cl
number of samples	65	68	68	37			44	43
r ²	0.92	0.94	0.91	0.89			0.80	0.88

Ionic predictors are listed in the order selected by the stepwise regression procedure. The negative (-) sign represents an inverse relationship between acidity and the specified ion.

*Daily samples from KSC13/NADP were used for the period January 1978 - October 1981. NADP samples collected weekly were used for 1984 and 1985 evaluations.

Table 6. Linear regression model of the relationship between various monthly weighted average concentrations in rain at UCF and KSC site 13/NADP.

		<u>r</u>	<u>n</u>
KSC	$H=1.143(NO_3) + 11.97$	0.580	73
UCF	$H=1.548(NO_3) + 4.29$	0.761	98
KSC	$H=0.545(xsSO_4) + 10.51$	0.628	73
UCF	$H=0.911(xsSO_4) + 1.34$	0.823	98
KSC	$Cl=1.107(Na) + 0.701$	0.991	73
UCF	$Cl=1.163(Na) + 0.519$	0.999	98
KSC	$Mg=0.233(Na) + 1.073$	0.979	73
UCF	$Mg=0.241(Na) + 0.570$	0.998	98
KSC	$NH_4=0.623(xsSO_4) - 6.979$	0.775	73
UCF	$NH_4=0.385(xsSO_4) + 0.62$	0.600	98
KSC	$NO_3=0.381(xsSO_4) + 1.572$	0.866	73
UCF	$NO_3=0.428(xsSO_4) + 2.554$	0.786	98

KSC data covers the period September 1977 - October 1981 and January 1984 - December 1985.

UCF data covers the period November 1977 - December 1985.

may be of some consequence when decisions on the construction of towers, buildings, and other structures must be made. Changes in vegetation due to acid rain may have long-term impacts on wildlife habitats at KSC. Groundwater contamination is a possibility and the acid deposition data may provide an additional source of input information. The data may also be of use in evaluations prior to the permitting of storm water discharges.

The data already accumulated from the NADP and UCF monitoring efforts provide a quality, relatively short-term data base for research in a number of areas such as watershed effects and materials effects and a start to the building of a long-term environmental data base.

For the present, the UCF and NADP sites are sufficient rain quality indicators for decision making purposes at KSC. Volume data collection should be continued where there is an interest (such as in the areas of the launch complexes, the Vehicle Assembly Building and the Shuttle Landing Facility) due to the spatial heterogeneity of rainfall volumes from events in central Florida.

Additional trend evaluation of precipitation data for KSC or UCF should be deferred until monitoring data which covers much longer time periods are available. This recommendation is based in part upon the variability that has been observed in the existing KSC/UCF data set. In addition, conclusions that have been drawn by different researchers who have evaluated 15 year data sets for acid deposition by Hubbard Brook and for the northeastern U.S. (USGS data) do not agree because of the approaches used to statistically evaluate the data sets. The discrepancies may occur because the different statistical tests for evaluation of trends have been applied dependent upon the background of the specific researcher. Evaluations which focus on temporal change in concentration instead of total deposition which is based on the product of concentration and rainfall amount also have yielded different conclusions. An acid deposition monitoring program which extends beyond 15 years would seem mandatory before extensive evaluation of trends is justified. It is likely that precipitation composition of UCF samples can continue to serve as an indicator of KSC precipitation composition once correction for the marine influence is incorporated.

V. LITERATURE CITED

- Bigelow, D.S. 1982. NADP instruction manual: site operation. National Atmospheric Deposition Program Report.
- Bigelow, D.S. 1984. Instruction manual: NADP/NTN site selection and installation. National Atmospheric Deposition Program Report.
- Bilonick, R.A. and D.G. Nichols. 1983. Temporal variations in acid precipitation over New York state - what the 1965-1979 USGS data reveal. Atmos. Environ. 17:1063-1072.
- Dreschel, T. 1984. A preliminary status report of rainfall monitoring at the Kennedy Space Center: review of data collected during the period of August 1983 through January 1984. Bionetics Contract Report.
- ESE. 1982. Florida acid deposition study. Environmental Science and Engineering, Inc.
- Galloway, J.N. and G.E. Likens. 1978. The collection of precipitation for chemical analysis. Tellus 30:71-82.
- Galloway, J.N. and G.E. Likens. 1981. Acid precipitation: the importance of nitric acid. Atmos. Environ. 15:1081-1085.
- Heaney, J.P., B. Koopman, D.S. Dwornick, and D.R. Salinwanchik. 1984. Water resources of the Kennedy Space Center. Final Report. Florida Resources Research Center. Publication No. 82, University of Florida, Gainesville.
- Hidy, G.M., D.A. Hansen, R.C. Henry, K. Ganesan, and J. Cullins. 1984. Trends in historical acid precursor emissions and their airborne and precipitation products. J. Air. Pollut. Control Assoc. 34:333-354.
- Jones, K.L. 1986. Quantitative assessment of storm water runoff from the Vehicle Assembly Building area of the John F. Kennedy Space Center, Florida. M.S. thesis (in preparation) Florida Institute of Technology, Melbourne, Florida.
- Keene, W.C. and J.N. Galloway. 1984. Organic acidity in precipitation in North America. Atmos. Environ. 19:199-202.
- Likens, G.E., F.H. Bormann, R.S. Pierce, J.S. Eaton, and R.E. Munn. 1984. Long-term trends in precipitation chemistry at Hubbard Brook, NH. Atmos. Environ. 18:2641-2647.
- Madsen, B.C. 1981. Kennedy Space Center precipitation monitoring program. Annual Contract Report.
- Madsen, B.C. 1981a. Acid rain at Kennedy Space Center Florida: recent observations. Atmos. Environ. 15:853-862.

- Madsen, B.C. 1982. Effect of sampling interval length on the composition of wet only deposition. Atmos. Environ. 16:2515-2519.
- Madsen, B.C. 1984. Comparison of wet deposition at coastal and inland sites in east-central Florida in deposition both wet and dry. Acid Precipitation Series, Vol. 4., Ed. B.B. Hicks Butterworth Publ.
- Madsen, B.C. 1985. Characterization and evaluation of acid rain at a site remote from the Kennedy Space Center. NASA/KSC Final Contract Report. April 1985.
- MAP3S/RAINE Research Community. 1982. The MAP3S/RAINE precipitation chemistry network: statistical overview for the period 1976-1980. Atmos. Environ. 16:1603-1631.
- NADP. 1984. Quality assurance plan-deposition monitoring. National Atmospheric Deposition Program.
- Pratt, G.C., M. Coscio, D.W. Gardner, B.I. Chevone, and S.V. Krupa. 1983. An analysis of the chemical properties of rain in Minnesota. Atmos. Environ. 17:347-355.
- Robinson, J.K. and J.W. Wilson. 1985. Design of the National Trends Network for monitoring the chemistry of atmospheric precipitation. U.S. Geological Survey Circular 964.
- Verry, E.S. 1983. Precipitation chemistry at the Marcell Experimental Forest in north-central Minnesota. Water Resour. Res. 19:454-462.

STANDARD TITLE PAGE

1. Report No.		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle An Evaluation of Rain Chemistry for the John F. Kennedy Space Center, Florida and the University of Central Florida, Orlando, Florida.				5. Report Date	
				6. Performing Organization Code BIO-1	
7. Author(s) Madsen, B.C. (1), T.W. Dreschel and C.R. Hinkle (2)				8. Performing Organization Report No.	
9. Performing Organization Name and Address (1) University of Central Florida Orlando, FL 32816 (2) The Bionetics Corp. John F. Kennedy Space Center KSC, FL 32899				10. Work Unit No.	
				11. Contract or Grant No. NAS10-10285	
12. Sponsoring Agency Name and Address NASA/John F. Kennedy Space Center, Florida 32899				13. Type of Report and Period Covered	
				14. Sponsoring Agency Code MD-RES	
15. Abstract Concern over the effects of Space Shuttle launches prompted the initiation of a rather intense environmental monitoring program in July 1977. The program included a precipitation monitoring network with 13 precipitation collection sites which were operated for various time periods to baseline precipitation chemistry at the John F. Kennedy Space Center (KSC). One additional site was also established as a remote background site on the University of Central Florida (UCF) campus near Orlando, 30 miles west of KSC. One of the 13 sites was converted to a National Atmospheric Deposition Program (NADP) station in August of 1983. Collections and analyses of samples were performed using a number of methodologies during the monitoring period. An evaluation of the data for comparability and utility for acid rain research was performed using the anion/cation, measured conductivity/calculated conductivity, Cl/Na, and Mg/Na ratios. Data collected at all KSC sites between 1977 and 1981, from 1983 to 1985 at the NADP site and at UCF to 1985 are comparable and appropriate for determining acid rain trends. Examination of those comparable data showed a fairly stable pH between 1977 and 1982 and an increase of 0.2 pH units which was observed as an incremental increase between 1982 and 1983 at KSC and UCF. The pH has remained again stable for 1984 and 1985. There is no indication of any adverse impacts from Shuttle impacts to rain chemistry.					
16. Key Words Acid Rain, Rain Chemistry, Atmospheric Deposition, Environmental Monitoring					
17. Bibliographic Control			18. Distribution Publicly Available		
19. Security Classif.(of this report) Unclassified		20. Security Classif.(of this page) Unclassified		21. No. of Pages 24	
22. Price					